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Triblock copolymer-based luminescent organic–inorganic hybrids triggered by heating and fluoroquinolone antibiotics

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ABSTRACT

The work introduces smart organic-inorganic hybrids with temperature- and substrate-induced quenching and sensitization of hexamolybdenum iodine cluster-centered luminescence based on iodine cluster salt $[K(diglyme)(CH_3CN)]_2[Mo_6I_{14}]$ (**1**) and triblock copolymer $(PEO)_{13}(PPO)_{30}(PEO)_{13}$ (L64). Formation of supramolecular assembly of $[Mo_6I_{14}]^{2-}$, K^+, and L64 molecules at fixed concentration conditions is manifested by specific cluster-centered luminescence. These supramolecular assemblies exhibit reversible luminescence quenching when temperature or concentration of L64 increases. The temperature-induced reversible aggregation of the L64-based organic-inorganic hybrids is followed by the reversible quenching of the cluster-centered luminescence. The ion-pairing equilibrium between the cluster anions and fluoroquinolones is shifted by the aggregation of the L64-based hybrids, which results in more enhanced quenching of the luminescence. These tendencies provide the route to sense the triblock copolymer-based phase transitions through the response of the cluster-centered luminescence.
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1. Introduction

Supramolecular systems able to give an active fluorescent response to external stimuli are of particular importance for analytical purposes [1–7]. Thermally triggered luminophores are of great importance for development of thermoresponsive materials [3,8]. Previously published papers [6,8] exemplify correlation of the temperature-induced phase transitions in liquid crystals and in aqueous solutions of triblock copolymers with lanthanide-centered luminescence. The development of water soluble supramolecular systems, where luminescence of inorganic luminophor correlates with thermally triggered aggregation of water soluble polymers is of particular importance, since it opens new routes to sense such phase transitions in aqueous solutions through a luminescent response.

The reason for choice of hexamolybdenum halide clusters with the $\{Mo_6X_8\}^{4+}$ core and six additional terminal ligands as the inorganic luminophor is based on its unique metal-centered luminescence [9–21]. The enhanced response of the clusters luminescence to dioxygen [17,18] makes them promising building blocks for fiber optic probes. It is worth noting that literature data highlight, first of all, the change of inner- and outer-sphere environment as a powerful tool to tune Mo-centered luminescence by an apical ligands substitution [14–16] and counter-ions exchange [19,21]. However, the applicability of apical ligands substitution methodology is restricted by low lability of the apical positions, which makes ligand exchange procedures rather time and energy consuming [22,23]. Fortunately, outer-sphere environment of the cluster anions is another significant factor affecting their luminescence. In this connection, introduction of suitable counter-ions [19–21] along with dioxygen [24] and/or water molecules as O–H oscillators [25] provide a workable opportunity to tune the cluster-centered luminescence, and create a more convenient basis than inner-sphere ligands exchange, for development of smart luminescent supramolecular systems. The paper [26] introduces mesogenic luminescent material, where hexanuclear molebdenum and rhenium clusters are incorporated into organic matrix through the ion-pairing with organic cations. Thus, connection of luminescent inorganic cluster units with organic amphiphiles

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